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(71) Applicant: 000228109 (Nippon Elastomer KK)
(71) Applicant: 000000033 (Asahi Chemical Industry Co., Ltd.)
(72) Inventor: Masahiro Fujiwara
(72) Inventor: Yoshihiro Inoki
(72) Inventor: Yoro Sasaki
(72) Inventor: Sugao Kato
(74) Agent: Takeshi Shimizu, Patent Attorney (and three others)
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(54) [Title of the Invention] **Thermoplastic Block Copolymer**

(57) [Abstract]

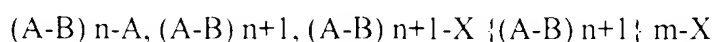
[Means] A thermoplastic block copolymer, comprising a polymer block A based on a hydrogenated vinyl aromatic hydrocarbon compound and a polymer block B based on a hydrogenated conjugated diene compound, wherein the pre-hydrogenation number average molecular weight of the vinyl aromatic hydrocarbon compound polymer of polymer block A is more than 14,000, the hydrogenation rate of the total aromatic rings, as determined by NMR, is at least 80%, while that of the total olefinic unsaturated double

bonds is at least 90%, the number average molecular weight decreases less than 10% after hydrogenation, and the pre-hydrogenation weight ratio of the vinyl aromatic hydrocarbon compound in the copolymer to the conjugated diene compound is between 10/90 and 90/10.

[Effect] The thermoplastic block copolymer has better heat resistance, formability, and physical properties such as strength than conventional products.

[Claims]

[Claim 1] A thermoplastic block copolymer represented by the following general formulas, comprising a block copolymer wherein the pre-hydrogenation number average molecular weight of the vinyl aromatic hydrocarbon compound polymer of polymer block A is more than 14,000, the hydrogenation rate of the total aromatic rings, as determined by NMR, is at least 80%, while that of the total olefinic unsaturated double bonds is at least 90%, the number average molecular weight decreases less than 10% after hydrogenation, and the pre-hydrogenation weight ratio of the vinyl aromatic hydrocarbon compound in the copolymer to the conjugated diene compound is between 10/90 and 90/10;



(where A is a polymer block based on a hydrogenated vinyl aromatic hydrocarbon compound; B is a polymer block based on a hydrogenated conjugated diene compound; X is a multifunctional coupler residue; and n and m is an integer of 1 or more).

[Claim 2] A thermoplastic block copolymer as set forth in Claim 1, wherein the pre-hydrogenation weight ratio of the vinyl aromatic hydrocarbon compound in the copolymer to the conjugated diene compound is between 10/90 to 50/50.

[Claim 3] A thermoplastic block copolymer as set forth in Claim 2, wherein the conjugated diene compound in the copolymer has 20 to 60 mol% side chains prior to hydrogenation.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Application]

The present invention relates to a thermoplastic block copolymer, and in particular to a thermoplastic hydrogenated block copolymer having a low molecular weight distribution, in which specific block copolymer unsaturated olefin components and aromatic rings are hydrogenated, but with virtually no decrease in the number average molecular weight during hydrogenation, resulting in a thermoplastic block copolymer characterized by extremely high strength, heat resistance, and formability.

[0002]

[Prior Art]

Block copolymers comprising vinyl aromatic hydrocarbon compounds and conjugated diene compounds have been widely used conventionally in fields involving elastic materials, improved resins, adhesives, transparent resins, and the like. Recently, the double bonds of conjugated dienes have been hydrogenated to produce saturated types, resulting in hydrogenated block copolymers with better heat resistance, which have been put to use in a wide range of applications such as improved resin materials and molded materials. Block copolymers with hydrogenated dienes and block copolymers consisting of isoprene compounds and butadiene (as the conjugated diene compound) and styrene compounds (as the vinyl aromatic hydrocarbon compound) are particularly used in various materials in the form of elastomers with good heat resistance, weatherability, strength, and flexibility, and in the form of resins with good transparency and impact resistance.

[0003]

Block copolymer compositions comprising a blend of such styrene block copolymers and their hydrogenated polymers with thermoplastic resins or the like are now being put to wider practical use in view of their even better heat resistance, fluidity, adhesion, and the like. The commercial demands made recently on such polymer materials have become increasingly sophisticated, however, with more and more pressure for even better heat resistance and formability. Conventional styrene-conjugated diene block copolymers are unlikely to meet such demands, and even block copolymers comprising hydrogenated dienes have resulted in a dramatic loss of physical properties at elevated temperatures. Efforts to increase the molecular weight to improve the physical properties have also resulted in a considerable loss of fluidity and formability.

[0004]

A method that has been considered for improving heat resistance is to also hydrogenate the aromatic rings of styrenes and to increase the T_g. Several such methods are already being studied. The Specification of US Patent 3,333,024, for example, describes examples for the hydrogenation of the unsaturated olefin components and the styrene aromatic rings of styrene-isoprene-styrene block copolymers of relatively low molecular weight, but there are no examples of high molecular weight block copolymers. Furthermore, the molecular chains are broken during hydrogenation in this method, resulting in block copolymers with considerably compromised physical properties.

[0005]

The Specifications of US Patent 5,352,744 and WO 96 34896 describe a method for the hydrogenation of the unsaturated olefin components and styrene aromatic rings of styrene-isoprene-styrene block copolymers of relatively low molecular weight, where the Tg of the styrene block has indeed been increased. However, no high molecular weight elastomers are described in the Specifications of these inventions. In addition, the styrene block has a low molecular weight before hydrogenation, and the heat resistance is not improved as much as in the present invention.

[0006]

In Japanese Unexamined Patent Application (Kokai) 3-160051, the hydrogenation of the unsaturated olefin components and styrene aromatic rings of styrene-butadiene block copolymers with a high styrene content results in better heat resistance, allowing the material to be developed into an optical material, but the hydrogenation that is described results in considerable cleavage of the molecular chains. The number average molecular weight decreases far more than 10% after the reaction, resulting in a block copolymer with little improvement in strength or other physical properties. At any rate, no block copolymers with higher heat resistance and formability are currently available, while a high molecular weight elastomer with better elasticity in particular has yet to be achieved.

[0007]

[Problems Which the Invention Is Intended to Solve]

In view of the prior art described above, an object of the present invention is to provide a thermoplastic block copolymer with better physical properties such as strength, heat resistance, and formability.

[0008]

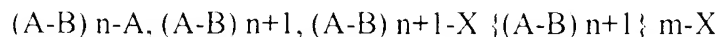
[Means for Solving the Abovementioned Problems]

As a result of extensive research to resolve the drawbacks described above, the inventors discovered that better heat resistance, fluidity, formability, and strength could be achieved with block copolymers when the unsaturated olefin components and aromatic rings of block copolymers of conjugated diene compounds and vinyl aromatic hydrocarbon compounds having a specific structure were characterized by a high degree of hydrogenation, with no cleavage of the molecular chains during hydrogenation. The

present invention was perfected upon the further surprising discovery that satisfactory formability was obtained with high molecular weight block copolymers having a vinyl aromatic hydrocarbon compound content of no more than 50% and a number average molecular weight of more than 200,000.

[0009]

That is, the present invention is a thermoplastic block copolymer represented by the following general formulas, comprising a block copolymer wherein the pre-hydrogenation number average molecular weight of the vinyl aromatic hydrocarbon compound polymer of polymer block A is more than 14,000, the hydrogenation rate of the total aromatic rings, as determined by NMR, is at least 80%, while that of the total olefinic unsaturated double bonds is at least 90%, the number average molecular weight decreases less than 10% after hydrogenation, and the pre-hydrogenation weight ratio of the vinyl aromatic hydrocarbon compound in the copolymer to the conjugated diene compound is between 10/90 and 90/10:



(where A is a polymer block based on a hydrogenated vinyl aromatic hydrocarbon compound; B is a polymer block based on a hydrogenated conjugated diene compound; X is a multifunctional coupler residue; and n and m is an integer of 1 or more).

[0010]

The present invention is described in detail below. The present invention is a thermoplastic block copolymer in which the unsaturated olefin component and aromatic rings of a block copolymer comprising a conjugated diene compound and a vinyl aromatic hydrocarbon compound having a specific structure are characterized by a high degree of hydrogenation, with substantially no cleavage of the molecular chains during hydrogenation. In the present invention, the pre-hydrogenation number average molecular weight of the vinyl aromatic hydrocarbon compound polymer of the block copolymer is more than 14,000. A lower molecular weight results in a block copolymer with less improvement in heat resistance. The present invention is also a block copolymer in which the number average molecular weight decreases less than 10% after hydrogenation. A greater decrease in the number average molecular weight results in considerable molecular chain cleavage, and thus in lower strength, elasticity, and the like.

[0011]

The present invention is described in further detail below. The block copolymer in the present invention comprises a polymer block A based on a hydrogenated vinyl aromatic hydrocarbon compound and a polymer block B based on a hydrogenated conjugated diene compound. Examples of vinyl aromatic hydrocarbon compounds include one or more selected from styrene, α -methylstyrene, p-methylstyrene, p-tert-butylstyrene and similar alkylstyrenes, and para-methoxystyrene, vinylnaphthalene, or the like, among which styrene is preferred.

[0012]

The polymer based on a vinyl aromatic hydrocarbon compound in the present invention includes cases comprising one or more vinyl aromatic hydrocarbon compounds as well as cases of copolymers thereof and other living anion polymer compounds. Examples of copolymerizable compounds include conjugated diene compounds, methyl methacrylate, butyl methacrylate and similar methacrylic acid esters, cyclohexanediene, caprolactones, and the like. The copolymer may be used in various forms, such as random, alternating, tapered, or other configurations. In cases of more than one polymer block A, the blocks may have different compositions, molecular weights, and so forth.

[0013]

As used herein, the expression "based on a vinyl aromatic hydrocarbon compound" means that the hydrogenated vinyl aromatic hydrocarbon compound accounts for at least 50 mol%, and preferably at least 70 mol%, of polymer block A. Examples of conjugated diene compounds include one or more selected from butadiene, isoprene, 1,3-cyclohexadiene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, and the like, among which butadiene, isoprene, and combinations thereof are preferred. The pre-hydrogenated conjugated diene compound block can have any microstructure. Polybutadiene blocks, for example, preferably have between 10 and 90 mol% side-chain 1,2 bonds. A range of between 20 and 60 mol% is particularly desirable for elastic material applications.

[0014]

As used herein, polymers based on conjugated diene compounds can include copolymers of other living anion compounds and conjugated diene compounds. Examples of such copolymerizable compounds include vinyl aromatic hydrocarbon compounds, methyl methacrylate, butyl methacrylate and similar methacrylic acid esters, cyclohexanediene, caprolactones, and the like. The copolymer may be used in various

forms, such as random, alternating, tapered, or other configurations. In cases of more than one polymer block B, the blocks may have different compositions, molecular weights, and so forth.

[0015]

As used herein, the expression "based on conjugated diene compounds" means that hydrogenated conjugated diene compounds account for at least 50 mol%, and preferably at least 70 mol%, of polymer block B. In the present invention, the vinyl aromatic hydrocarbon polymer contained in polymer block A has a pre-hydrogenation weight of more than 14,000. 14,000 or less results in a lower T_g after hydrogenation of the aromatic rings as well as in less improvement in heat resistant strength at elevated temperatures, which would be commercially unsatisfactory. Although there is no maximum molecular weight in particular, a weight of more than 500,000 will afford satisfactorily improved heat resistance but sometimes suffers from poor formability.

[0016]

In terms of polystyrene, the block copolymer of the present invention preferably has a number average molecular weight of at least 35,000. Although there is no maximum molecular weight in particular, the weight is preferably no more than 600,000, and even more preferably between 50,000 and 400,000. 35,000 results in lower strength and elasticity, whereas more than 600,000 results in satisfactory improvement in heat resistance but occasionally poor formability.

[0017]

The structure of the block copolymer in the present invention may be linear, branched, radial, pectinate, a combination thereof, or the like. Preferred structures include A-B-A, A-B-A-B, and (A-B)₄-X. Also included are tapered polymers in which the borders between blocks start out as random copolymers, but the composition of which gradually changes.

[0018]

The weight ratio of the vinyl aromatic hydrocarbon compound to conjugated diene compound in the block copolymer before hydrogenation in the present invention may range from 10/90 to 90/10. A vinyl aromatic hydrocarbon compound content of less than 10% does not improve heat resistance, whereas more than 90% results in low impact resistance. Particularly for elastic material applications, a weight ratio of between 10/90

and 50/50 affords a good balance of heat resistance, strength, formability, and elasticity, although a range of 20/80 to 40/60 results in even better elastic materials.

[0019]

At least 80%, and preferably at least 90%, of the total aromatic rings in the block copolymer of the present invention are hydrogenated, while at least 90%, and preferably at least 95%, of the total olefinic unsaturated double bonds are hydrogenated. When the hydrogenation rate of the total olefinic unsaturated double bonds is less than 90%, heat and light can cause considerable deterioration, leading to a loss of thermoplasticity and other physical properties. When the hydrogenation rate of the total aromatic rings is less than 80%, the result is a lower T_g, and poor heat resistance, strength, and formability. The hydrogenation rate can be determined by NMR.

[0020]

In the block copolymer of the present invention, the decrease in the number average molecular weight after hydrogenation must be less than 10%, preferably less than 5%, and even more preferably less than 3 %. When the number average molecular weight decreases more than 10% after hydrogenation, the considerable cleavage of the molecular chains during hydrogenation results in a loss of physical properties, particularly elastic properties such as strength and elongation set, and does not allow the effects of the invention to be achieved. The decrease in the number average molecular weight after hydrogenation can be determined by gel permeation chromatography (GPC).

[0021]

Examples for manufacturing pre-hydrogenated block copolymers can be found in Japanese Examined Patent Applications (Kokoku) 36-19286, 43-14979, and 49-36957. In these methods, an organic lithium compound or the like is used as an anion polymerization initiator in a hydrocarbon solvent, an ether compound such as diethyl ether or tetrahydrofuran or a tertiary amine such as triethylamine or tetramethylethylenediamine is added, the amount and type of the side-chain bonds of the conjugated diene compound block are controlled, and a multifunctional compound such as silicon tetrachloride or epoxified soybean oil is used as a coupling agent if needed to bring about the block polymerization of a vinyl aromatic hydrocarbon compound and a conjugated diene compound, resulting in a pre-hydrogenated block copolymer with a linear, branched, or radial structure.

[0022]

An example of a method for hydrogenating block copolymers is the single stage hydrogenation of the aromatic rings of vinyl aromatic hydrocarbon compounds and the olefinic double bonds of the conjugated diene compounds in block copolymers. For example, a metal catalyst of Pd, Rh, or the like supported on an alumina carrier may be added in an amount of between 1 and 100 wt% relative to the block copolymer in a hydrocarbon solvent, and the reaction may be brought about at a temperature of between 120 and 250°C, and preferably between 130 and 220°C, and a hydrogen partial pressure of 2 MPa to 25 MPa, and preferably 3 MPa to 20 MPa. Following the conclusion of the reaction, the catalyst is preferably separated by a common method and recycled. In a two stage method of hydrogenation, the olefinic double bonds of conjugated diene compounds in block copolymers are first hydrogenated by a common method, and the aromatic rings of vinyl aromatic hydrocarbon compounds are then hydrogenated by the method described above. The single stage method is preferred, however, in view of its ease of processing, productivity, and so forth.

[0023]

Inorganic fillers, stabilizers, lubricants, colorants, silicone oils, mineral oils, flame retardants, and the like can be added as needed to the block copolymer of the present invention. Examples of inorganic fillers include calcium carbonate, magnesium carbonate, talc, magnesium hydroxide, mica, barium sulfate, white carbon, titanium oxide, and carbon black. Examples of stabilizers include hindered phenol antioxidants, phosphate heat stabilizers, hindered amine photostabilizers, and benzotriazole UV absorbents. Examples of lubricants include stearic acid, stearic acid esters, stearic acid amides, and stearic acid metal salts. Examples of mineral oils include paraffin components, naphthene components, and aromatic components, in any proportion. Any mixer such as a Banbury mixer, Labo Plastomill, single-screw extruder, or twin-screw extruder can be used to mix the aforementioned components and the block copolymer of the present invention.

[0024]

[Embodiments of the Invention]

The present invention is described in further detail below with reference to examples, but the present invention is in no way limited to these examples alone.

[Examples]

Analysis of Block Copolymer and Evaluation of Physical Properties

Quantification of block copolymer styrene content:

The absorbance of a chloroform solution of the block copolymer was determined using a UV spectrophotometer, and the styrene content of the block copolymer was determined based on a calibration curve of the predetermined relationship between styrene content and absorbance.

[0025]

Block copolymer molecular weight and pre-hydrogenation styrene block chain length:

The weight was calculated by gel permeation chromatography (GPC) using commercially available reference polystyrene for the preparation of GPC calibration curves. The pre-hydrogenation styrene block chain length was determined from styrene blocks obtained by the osmium acid decomposition of block copolymers in chloroform before hydrogenation.

Hydrogenation rate of block copolymer: This was determined from H-NMR spectra.

Melt flow rate (MFR): This was determined at a load of 2.16 kg and at a temperature of 230°C in accordance with JIS K 7210.

[0026]

Hardness: This was determined in accordance with JIS K6301 (type A).

Breaking strength and elongation: In accordance with JIS K 6301, the samples used were 2 mm thick compression molded sheets, and the test pieces were No. 3 dumbbells.

Elongation set: In accordance with JIS K 6301, the samples used were 2 mm thick compression molded sheets, and the test pieces were No. 3 dumbbells. The residual strain after 100% elongation was measured.

Impact resilience: This was determined using a Dunlop tripsometer. The samples were 4 mm thick compression molded sheets.

[0027] Polymerization of Block Copolymers

620 g styrene, 65 g tetrahydrofuran, and 26 L of dried and purified cyclohexane were charged into a 40 L autoclave under nitrogen, the contents were heated to 60°C, cyclohexane solution containing 2.7 g n-butyl lithium was added, polymerization was initiated, the polymerization of the styrene was concluded, 1940 g butadiene was then added, the polymerization was concluded, another 620 g styrene was added, and the polymerization was concluded, giving a tri-block copolymer (SBS) (block copolymer A-1) with a number average molecular weight of 106,000, a styrene content of 39%, and a styrene block chain length of 15,200, with 32 mol% butadiene side-chains.

[0028]

The various pre-hydrogenated block copolymers (A-1 through A-7) shown in Table 1 were obtained by polymerization in the same manner as above except for variations in the amounts of tetrahydrofuran, n-butyl lithium, styrene, and butadiene that were added, and in some cases the sequential polymerization of styrene, butadiene, styrene, and butadiene, in that order, to produce tetra-block copolymers. 990 g styrene, 88 g tetrahydrofuran, and 26 L of dried and purified cyclohexane were charged into a 40 L autoclave under nitrogen, the contents were heated to 60°C, cyclohexane solution containing 3.5 g n-butyl lithium was added, polymerization was initiated, the polymerization of the styrene was concluded, 2210 g butadiene was then added, the polymerization was concluded, 2.2 g silicon tetrachloride was added, and the coupling reaction was concluded, giving a radial tri-block copolymer ((SB4)-Si+SB, A-8) with a number average molecular weight of 320,000, a styrene content of 31%, and a styrene block chain length of 16,900, with 38 mol% butadiene side-chains.

[0029]

[Table 1]

Block copolymer before hydrogenation	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8
Block structure	SBS	SBS	SBS	SBSB	SBS	SBS	SBSB	(SB4)-Si SB (95:5)
Num. ave. mol. wt.	10600 0	14000 0	22200 0	23100 0	71000 4000	10100 0	11500 0	(SB4)-Si:320000
Mol. wt. distribution	1.03	1.04	1.05	1.06	1.03	1.03	1.03	1.11
Styrene content (%)	49.37	34	33	20	80	30	20	31
Polystyrene block num. ave. mol. wt.	15200	16300 0	25000	14900	28000	10200 0	7300	16900
Butadiene side chains (mol%)	32	45	37	40	35	40	40	38

[0030] Example 1

1200 g of a cyclohexane solution of 13.5 wt% block copolymer A-1 (the terminal growth of which had been stopped with the addition of methanol in an amount of 1.2 equivalents relative to Li following the conclusion of polymerization) was charged into a 2 L autoclave, 48 g of 5% palladium-alumina powder (particle diameter: 20 microns) mfg. by N. E. Chemcat was added, the system was then placed under nitrogen and heated to 180°C, and hydrogenation was brought about for 6 hours at a hydrogen pressure of 8.3 MPa, giving a hydrogenated block copolymer with 100% hydrogenation of the unsaturated olefin component, 99.4% hydrogenation of the aromatic rings, a post-hydrogenation polymer number average molecular weight of 104,000 (representing a 1.9% decrease in number average molecular weight compared to before hydrogenation), and a molecular weight distribution of 1.03.

[0031] Example 2

Hydrogenation was brought about in the same manner as in Example 1 using block copolymer A-2, giving a hydrogenated block copolymer with 100% hydrogenation of the unsaturated olefin component, 99.2% hydrogenation of the aromatic rings, a post-hydrogenation polymer number average molecular weight of 138,000 (representing a 1.4% decrease in number average molecular weight compared to before hydrogenation), and a molecular weight distribution of 1.04.

[0032] Example 3

Hydrogenation was brought about in the same manner as in Example 1 using block copolymer A-3, except that the 5% palladium-aluminum powder was added in an amount of 96 g, giving a hydrogenated block copolymer with 99.8% hydrogenation of the unsaturated olefin component, 99.3% hydrogenation of the aromatic rings, a post-hydrogenation polymer number average molecular weight of 217,000 (representing a 2.4% decrease in number average molecular weight compared to before hydrogenation), and a molecular weight distribution of 1.05.

[0033] Example 4

Hydrogenation was brought about in the same manner as in Example 3 using block copolymer A-4, giving a hydrogenated block copolymer with 99.7% hydrogenation of the unsaturated olefin component, 99.2% hydrogenation of the aromatic rings, a post-hydrogenation polymer number average molecular weight of 226,000 (representing a 2.2% decrease in number average molecular weight compared to before hydrogenation), and a molecular weight distribution of 1.05.

[0034] Example 5

Hydrogenation was brought about in the same manner as in Example 3 using block copolymer A-8, giving a hydrogenated block copolymer with 99.7% hydrogenation of the unsaturated olefin component, 99.2% hydrogenation of the aromatic rings, a post-hydrogenation polymer number average molecular weight of 315,000 (representing a 1.6% decrease in number average molecular weight compared to before hydrogenation), and a molecular weight distribution of 1.11.

[0035] Comparable Example 1

Hydrogenation was brought about for 4.8 hours at 160°C by the same method as in Example 1 using block copolymer A-1, giving a partially hydrogenated block copolymer with 99.4% hydrogenation of the unsaturated olefin component and 62.6% hydrogenation of the aromatic rings.

[0036] Comparable Example 2

Hydrogenation was brought about for 3.6 hours at 160°C by the same method as in Example 1 using block copolymer A-2, giving a partially hydrogenated block copolymer with 99.3% hydrogenation of the unsaturated olefin component and 41.2% hydrogenation of the aromatic rings.

[0037] Comparative Example 3

Hydrogenation was brought about in the same manner as in Example 1 using block copolymer A-2, except that 5% ruthenium-alumina powder (particle diameter: 20 microns) mfg. by N. E. Chemcat was used instead of the 5% palladium-aluminum powder, giving a hydrogenated block copolymer with 100% hydrogenation of the unsaturated olefin component, 98.8% hydrogenation of the aromatic rings, a post-hydrogenation polymer number average molecular weight of 121,000 (representing a 13.6% decrease in number average molecular weight compared to before hydrogenation), and a molecular weight distribution of 1.20.

[0038] Comparative Example 4

Hydrogenation was brought about in the same manner as in Example 1 using block copolymer A-3, except that 200 g of 65% nickel-diatomaceous earth mfg. by Nissan Gadora was used instead of the 5% palladium-aluminum powder, giving a hydrogenated block copolymer with 100% hydrogenation of the unsaturated olefin component, 98.6% hydrogenation of the aromatic rings, a post-hydrogenation polymer number average molecular weight of 174,000 (representing a 21.6% decrease in number average molecular weight compared to before hydrogenation), and a molecular weight distribution of 1.31.

[0039] Comparative Example 5

Hydrogenation was brought about in the same manner as in Example 1 using block copolymer A-6, giving a hydrogenated block copolymer with 100% hydrogenation of the unsaturated olefin component, 99.6% hydrogenation of the aromatic rings, a post-hydrogenation polymer number average molecular weight of 100,500 (representing a 0.5% decrease in number average molecular weight compared to before hydrogenation), and a molecular weight distribution of 1.03.

Hydrogenation was brought about in the same manner as in Example 1 using block copolymer A-7, giving a hydrogenated block copolymer with 100% hydrogenation of the unsaturated olefin component, 99.6% hydrogenation of the aromatic rings, a post-hydrogenation polymer number average molecular weight of 114,000 (representing a 0.9% decrease in number average molecular weight compared to before hydrogenation), and a molecular weight distribution of 1.03. Table 2 gives the results obtained in the evaluation of the physical properties.

[0041]

[Table 2]

	Examp e 1	Examp e 2	Examp e 3	Examp e 4	Examp e 5	Comp Ex. 1	Comp Ex. 2	Comp Ex. 3	Comp Ex. 4	Comp Ex. 5	Comp Ex. 6
Block copolymer	A-1	A-2	A-3	A-4	A-8	A-1	A-2	A-2	A-3	A-6	A-7
Butadiene hydrogenation rate (%)	100	100	99.8	99.7	99.8	99.4	99.3	100	100	100	100
Aromatic ring hydrogenation rate (%)	99.4	99.2	99.3	99.2	99.4	62.6	41.2	98.8	98.6	99.6	99.7
Decrease in number average molecule weight	1.9	1.4	2.3	2.2	1.6	1.7	1.2	13.6	21.6	0.5	0.9
Molecular weight distribution	1.03	1.04	1.05	1.05	1.11	1.03	1.04	1.20	1.31	1.03	1.03
MFR (g/10 min)	0.37	0.10	0.01	0.08	0.02	0.12	0.008	0.27	0.04	1.24	7.33
Hardness (JIS A)	96	94	92	63	83	92	90	69	86	88	77
Breaking strength (kgf/cm ²)	490	360	415	370	340	390	305	240	210	310	230
Breaking elongation (%)	470	560	560	640	710	470	570	600	630	670	720
100% elongation on set (%)	13	8	10	11	8	12	8	11	14	12	9
Impact resilience (%)	64	47	48	59	56	62	48	41	42	49	67
Breaking strength at 90°C (kgf/cm ²)	180	185	230	190	205	75	60	90	85	70	35

[0042]

At least 90% hydrogenation of aromatic rings results in block copolymers with vastly improved heat resistance, extremely high tensile strength at elevated temperatures, far greater fluidity, and far better formability. The comparative examples show that block copolymers with a pre-hydrogenation styrene block chain length within the range of the present invention but a lower aromatic ring hydrogenation rate, as well as block copolymers with virtually completely hydrogenated aromatic rings but a styrene block chain length of 14,000 or less, had lower heat resistance, extremely low tensile strength at elevated temperatures, and a tendency to deform or become sticky. A low aromatic ring hydrogenation rate resulted in less improvement in fluidity and in a poor balance of physical properties. Block polymers with a substantial decrease in number average molecular weight following hydrogenation tended to undergo drastic chain cleavage during hydrogenation, resulting in a loss of physical properties, particularly strength, elongation set, and impact resilience, thereby precluding the effects of the present invention.

[0043] Example 6

Hydrogenation was brought about in the same manner as in Example 1 using block copolymer A-5, giving a hydrogenated block copolymer with 100% hydrogenation of the unsaturated olefin component, 99.7% hydrogenation of the aromatic rings, a post-hydrogenation polymer number average molecular weight of 70,600 (representing a 0.6% decrease in number average molecular weight compared to before hydrogenation), and a molecular weight distribution of 1.03. This thermoplastic block copolymer had dramatically improved heat resistance and formability.